Structural and Co-Conformational Effects of Alkyne-Derived Subunits in Charged Donor-Acceptor [2]Catenanes

Ognjen Š. Miljanić,[†] William R. Dichtel,[†,‡] Saeed I. Khan,[†] Shahab Mortezaei,[†] James R. Heath,[‡] and J. Fraser Stoddart[†]*

† California NanoSystems Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095

‡ Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125

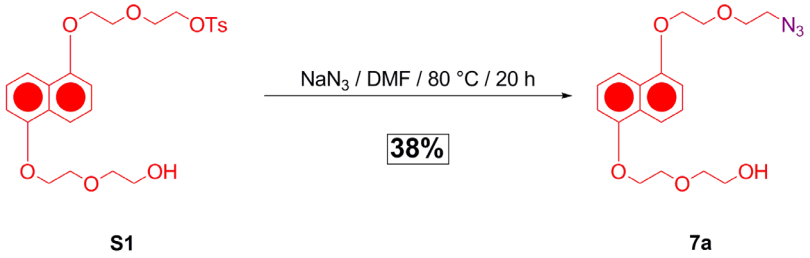
Supporting Information

REVISED VERSION

Correspondence Address
Professor J Fraser Stoddart California NanoSystems Institute and Department of Chemistry and Biochemistry University of California, Los Angeles 405 Hilgard Avenue Los Angeles, CA 90095-1569 (USA) Tel: (+1)-310-206-7078 Fax: (+1)-310-206-1843 Email: stoddart@chem.ucla.edu

General Methods. All reagents were purchased from commercial suppliers (Aldrich or Fisher) and used without further purification. Cyclobis(paraquat-*p*-phenylene) hexafluorophosphate[S1] (**CBPQT** · $4PF_6$), 1,5-bis[2-(2-hydroxyethoxy)ethoxy)] naphthalene[S2] (**6a**), 1,5-bis[2-(2-(2-hydroxyethoxy)ethoxy)ethoxy]naphthalene[S3] (**6b**), 1,5-bis[2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethoxy]naphthalene[S3] (**6c**) and mono-tosylates[S4,S5] of **6a** **(S1)** and **6b** were prepared according to literature procedures. Preparation and characterization of catenanes **1b** · $4PF_6$ and **2b** · $4PF_6$, and their precursors **7b**, **8b**, and **9b** was reported in a previous publication.[S6] Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (E. Merck). Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Melting points were recorded on an Electrothermal 9100 instrument in open capillary tubes and are uncorrected. Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance 400 and 500 spectrometers, with working frequencies of 400 and 500 MHz for ^1H, and 100 and 125 MHz for ^{13}C nuclei respectively. VT-NMR spectra were recorder on a Bruker Avance 500 spectrometer and temperature-calibrated using neat MeOH (for $T < 295$ K) and ethylene glycol (for $T > 295$ K). Chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents ($CDCl_3$: δ7.26 ppm, CD_3CN: δ1.93 ppm, DMF-d_7: δ 8.01 ppm). All ^{13}C spectra were recorded with the simultaneous decoupling of proton nuclei. Fast atom bombardment mass spectra were obtained on a JEOL JMS-600H high resolution mass spectrometer equipped with a FAB probe.

Scheme S1. Synthesis of DNP Azide Derivative **7a**.

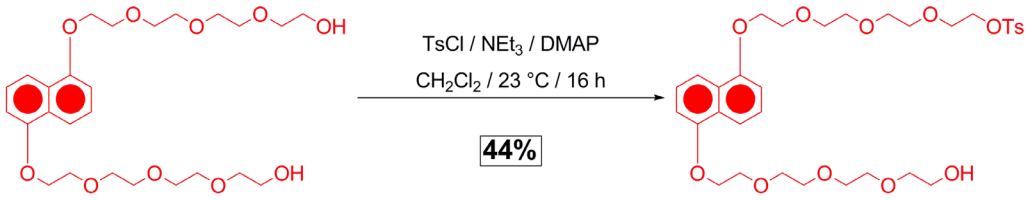


S1 **7a**

A solution of tosylate[S4] **S1** (1.37 g, 2.78 mmol) and NaN_3 (904 mg, 13.9 mmol) in dry DMF (15 mL) was heated at 80 °C for 20 h. After cooling, the solvent was removed in

vacuo. The resulting brown oil was redissolved in CH_2Cl_2, and washed first with 1M aqueous HCl solution, followed by sat. aqueous $NaHCO_3$ solution. After drying ($MgSO_4$) and removal of the solvent, the crude product was subjected to chromatography on silica (EtOAc → EtOAc/Me_2CO = 50/50) to provide 380 mg of **7a** as a viscous yellow oil (38%). **7a**: MS (FAB+): *m/z* (rel intensity) = 361 (M^+, 100%), 227 (39), 160 (36), 149 (79). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, ^3J (H,H) = 8.2 Hz, 1H), 7.87 (d, ^3J (H,H) = 8.2 Hz, 1H), 7.35 (t, ^3J (H,H) = 8.2 Hz, 1H), 7.35 (t, ^3J (H,H) = 8.2 Hz, 1H), 6.82 (d, ^3J (H,H) = 8.2 Hz, 1H), 6.80 (d, ^3J (H,H) = 8.2 Hz, 1H), 4.28–4.20 (m, 4H), 3.96–3.90 (m, 4H), 3.78–3.76 (m, 2H), 3.75–3.72 (br m, 2H), 3.68–3.65 (m, 2H), 3.39 (t, ^3J (H,H) = 5.0 Hz, 2H), 2.62 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.16 (2C), 126.65, 126.63, 125.15, 125.07, 114.60, 114.48, 105.70, 105.68, 72.58, 70.22, 69.69, 69.58, 67.82, 67.76, 61.64, 50.67. HRMS Calcd for $C_{18}H_{23}N_3O_5$: 361.1638. Found: 361.1649.

Scheme S2. Synthesis of DNP Monotosylate **S2**.

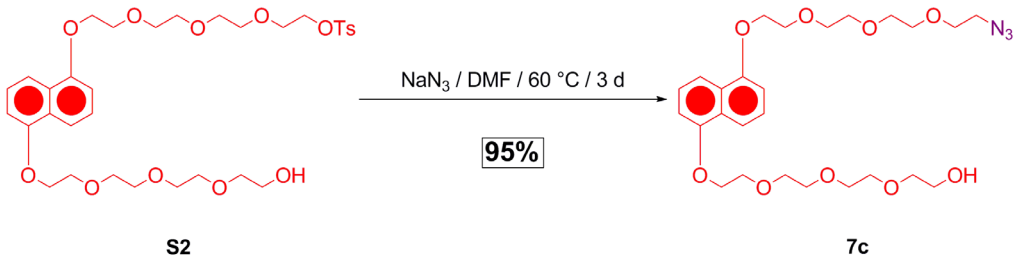


6c **S2**

The diol **6c** (1.38 g, 2.69 mmol), NEt_3 (555 mg, 780 µL, 5.50 mmol), and DMAP (20 mg, 0.16 mmol) were dissolved in CH_2Cl_2 (50 mL). A solution of TsCl (514 mg, 2.71 mmol) in CH_2Cl_2 (18 mL) was added dropwise to this mixture during 12 h at 23 °C (syringe pump, 1.5 mL/h). After the addition was complete, the reaction mixture was left to stir at 23 °C for 4 additional h. It was then washed with sat. aqueous $NaHCO_3$ solution and brine and dried ($MgSO_4$). Column chromatography (CH_2Cl_2 → EtOAc) isolated, in order of elution, the ditosylate[S3] of **6c** (310 mg, 17%), followed by **S2** (780 mg, 44%), and unreacted starting material (400 mg, 29%). **S2**: MS (FAB+): *m/z* (rel intensity) = 666 (M^+, 100%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, ^3J (H,H) = 8.4 Hz, 1H), 7.74 (d, ^3J (H,H) = 8.4 Hz, 1H), 7.61 (d, ^3J (H,H) = 8.0 Hz, 2H), 7.21 (t, ^3J (H,H) = 8.4 Hz, 1H), 7.21 (t, ^3J (H,H) =

8.4 Hz, 1H), 7.12 (d, ^{3}J (H,H) = 8.0 Hz, 2H), 6.68 (d, ^{3}J (H,H) = 8.4 Hz, 1H), 6.68 (d, ^{3}J (H,H) = 8.4 Hz, 1H), 4.11–4.07 (m, 4H), 3.97–3.94 (t, ^{3}J (H,H) = 4.4 Hz, 2H), 3.81–3.77 (m, 4H), 3.62–3.58 (m, 4H), 3.55–3.51 (m, 4H), 3.50–3.46 (m, 8H), 3.41–3.92 (m, 4H), 3.37–3.35 (m, 2H), 3.13 (br s, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.26 (2C), 144.76, 132.84, 129.80, 127.78, 126.64 (2C), 125.11 (2C), 114.51 (2C), 105.64 (2C), 72.49, 70.76 (2C), 70.52, 70.49, 70.48, 70.45, 70.38, 70.16, 69.63 (2C), 69.37, 68.46, 67.83 (2C), 61.43, 21.45. HRMS Calcd for $C_{33}H_{46}O_{12}S$: 666.2710. Found: 666.2693.

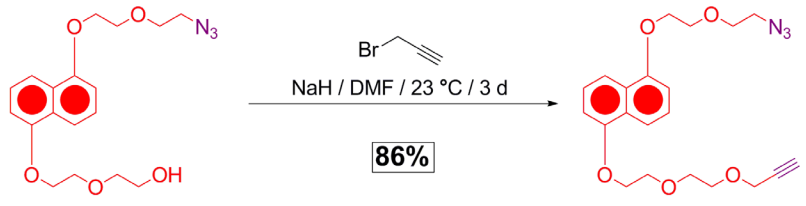
Scheme S3. Synthesis of DNP Azide Derivative **7c**.



S2 **7c**

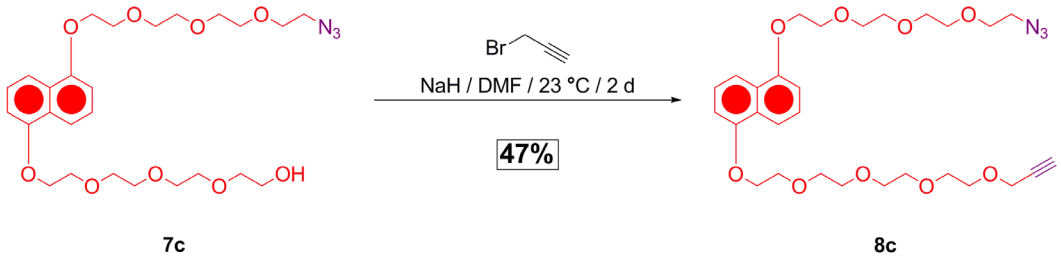
The tosylate **S2** (780 mg, 1.17 mmol) and NaN_3 (130 mg, 2.00 mmol) were dissolved in dry DMF (50 mL). The mixture was stirred at 60 °C for 3 d. After cooling, the solvent was removed in vacuo, and the crude material was filtered through a plug of silica, eluting with Me_2CO. A brown oil was obtained and found to be pure **7c** (599 mg, 95%). **7c**: MS (FAB+): *m/z* (rel intensity) = 537 (M^+, 100%), 510 (28). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (br d, ^{3}J (H,H) = 8.4 Hz, 2H), 7.27 (br t, ^{3}J (H,H) = 8.4 Hz, 2H), 6.75 (br d, ^{3}J (H,H) = 8.4 Hz, 2H), 4.20–4.18 (m, 4H), 3.91–3.88 (m, 4H), 3.73–3.70 (m, 4H), 3.64–3.58 (m, 8H), 3.56–3.53 (m, 8H), 3.50–3.48 (m, 2H), 3.27–3.24 (m, 2H), 3.09 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.30, 154.27, 126.71, 126.70, 125.13, 125.11, 114.60, 114.55, 105.70, 105.66, 72.54, 70.89, 70.81, 70.66, 70.58, 70.55, 70.50, 70.48, 70.16, 69.91, 69.71 (2C), 67.86 (2C), 61.47, 50.58. HRMS Calcd for $C_{26}H_{39}N_3O_9$: 537.2686. Found: 537.2684.

Scheme S4. Synthesis of DNP Azidoalkyne Derivative **8a**.



Compound **7a** (380 mg, 1.05 mmol) was dissolved in dry DMF (30 mL) and treated with NaH (60 mg, 2.10 mmol). After the evolution of gas ceased (~30 min), propargyl bromide (230 µL of 80% wt solution in PhMe, 2.10 mmol) was added via a syringe. The mixture was left to stir at 23 °C for 3 d. Solvent was removed in vacuo and the crude mixture was subjected to column chromatography (CH_2Cl_2/MeOH = 95/5). The first fraction contained **8a** as a brown oil (350 mg, 86%). **8a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, ^3J (H,H) = 8.4 Hz, 1H), 7.87 (d, ^3J (H,H) = 8.4 Hz, 1H), 7.37 (t, ^3J (H,H) = 8.4 Hz, 2H), 6.85 (d, ^3J (H,H) = 8.4 Hz, 1H), 6.85 (d, ^3J (H,H) = 8.4 Hz, 1H), 4.29–4.27 (m, 4H), 4.22 (d, ^4J (H,H) = 2.5 Hz, 2H), 3.99–3.96 (m, 4H), 3.82–3.77 (m, 6H), 3.41 (t, ^3J (H,H) = 5.0 Hz, 4H), 2.44 (t, ^4J (H,H) = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.35, 154.26, 126.77 (2C), 125.20, 125.12, 114.77, 114.58, 105.79, 105.75, 79.69, 74.66, 70.77, 70.37, 69.84 (2C), 69.22, 67.96, 67.94, 58.47, 50.82.

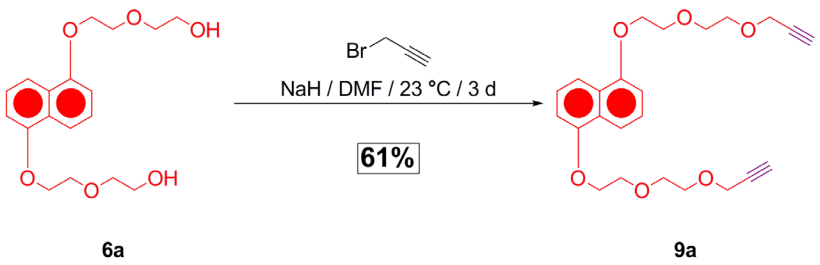
Scheme S5. Synthesis of DNP Azidoalkyne Derivative **8c**.



Compound **7c** (599 mg, 1.12 mmol) was dissolved in dry DMF (25 mL) and treated with NaH (48 mg, 2.00 mmol). After the evolution of gas ceased (~30 min), propargyl bromide (334 µL of 80% wt solution in PhMe, 3.00 mmol) was added via a syringe. The mixture was stirred for 2 d at 23 °C and subsequently quenched with MeOH (2.0 mL). Solvents

were removed in vacuo and the resulting crude mixture was filtered through a plug of silica (eluting with Me_2CO), and subsequently subjected to chromatography (CH_2Cl_2/Me_2CO = 75/25) to provide pure **8c** as the second fraction (300 mg, 47%). **8c**: MS (FAB+): *m/z* (rel intensity) = 575 (M^+, 94%), 548 (28), 537 (100), 510 (30). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (br d, ^3J (H,H) = 8.4 Hz, 2H), 7.34 (t, ^3J (H,H) = 8.4 Hz, 2H), 6.83 (d, ^3J (H,H) = 8.4 Hz, 2H), 4.29 (t, ^3J (H,H) = 5.0 Hz, 4H), 4.18 (d, ^4J (H,H) = 2.5 Hz, 2H), 3.99 (t, ^3J (H,H) = 5.0 Hz, 4H), 3.81–3.77 (m, 4H), 3.71–3.67 (m, 4H), 3.67–3.63 (m, 14H), 3.34 (t, ^3J (H,H) = 5.0 Hz, 4H), 2.41 (t, ^4J (H,H) = 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.25 (2C), 126.69 (2C), 124.95 (2C), 114.53 (2C), 105.58 (2C), 79.58, 74.37, 70.90, 70.88, 70.68, 70.62 (2C), 70.60, 70.54, 70.51, 70.29, 69.89, 69.71 (2C), 69.00, 67.83 (2C), 58.27, 50.56. HRMS Calcd for $C_{29}H_{41}N_3O_9$: 575.2842. Found: 575.2826.

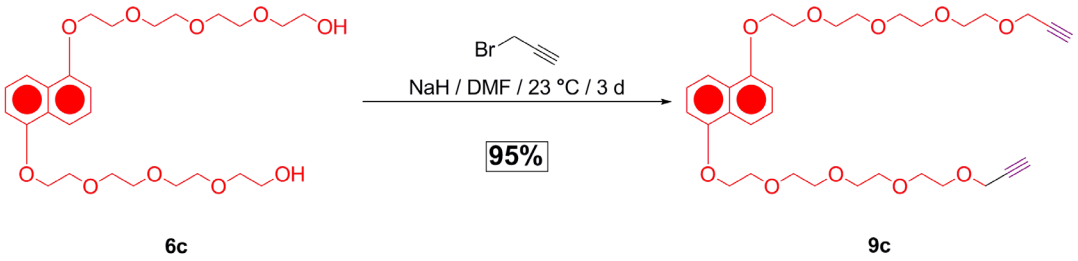
Scheme S6. Synthesis of DNP Diyne Derivative **9a**.



6a **9a**

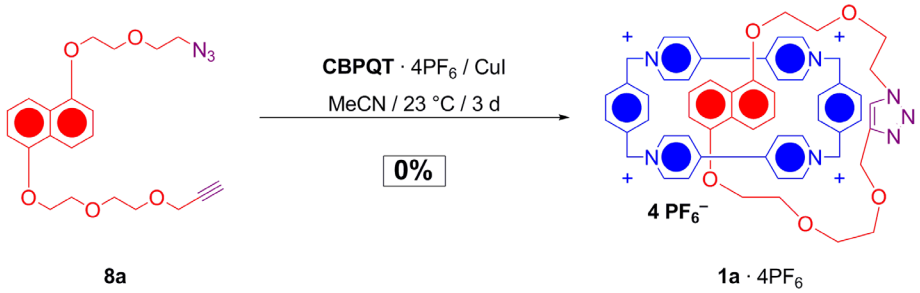
Diol **6a** (1.12 g, 3.33 mmol) was dissolved in dry DMF (25 mL) and treated with NaH (192 mg, 8.00 mmol). After the evolution of gas ceased (~30 min), propargyl bromide (2.2 mL of 80% wt solution in PhMe, 20.0 mmol) was added via a syringe. The mixture was stirred at 23 °C for 3 d. MeOH (2.0 mL) was added and the solvents were removed in vacuo. Crude brown oil was filtered through a plug of silica, eluting with Me_2CO, to provide pure **9a** (840 mg, 61%) as a dark yellow oil which solidifies on standing, mp 85–88 °C. **9a**: MS (FAB+): *m/z* (rel intensity) = 412 (M^+, 100%), 374 (16). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, ^3J (H,H) = 8.4 Hz, 2H), 7.21 (t, ^3J (H,H) = 8.4 Hz, 2H), 6.68 (d, ^3J (H,H) = 8.4 Hz, 2H), 4.11–4.09 (m, 4H), 4.06 (d, ^4J (H,H) = 2.4 Hz, 4H), 3.81–3.79 (m, 4H), 3.65–3.62 (m, 4H), 3.58–3.55 (m, 4H), 2.40 (t, ^4J (H,H) = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.21, 126.64, 125.08, 114.53, 105.64, 79.66, 74.80, 70.56, 69.66, 69.06, 67.80, 58.28. HRMS Calcd for $C_{24}H_{28}O_6$: 412.1886. Found: 412.1875.

Scheme S7. Synthesis of DNP Diyne Derivative **9c**.



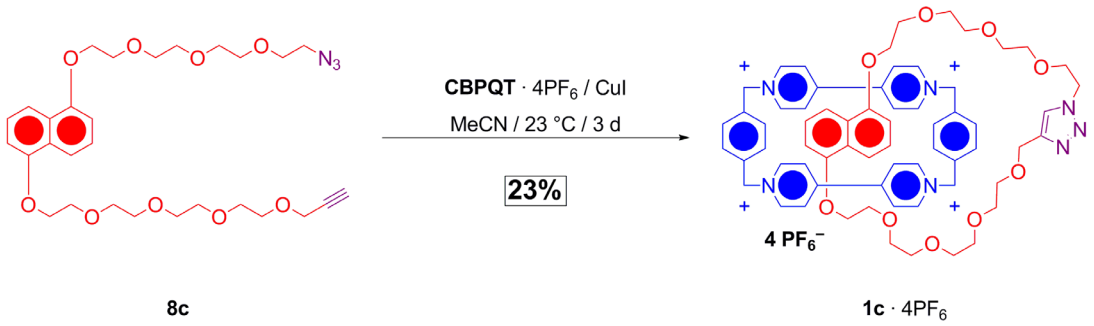
Diol **6c** (1.28 g, 2.50 mmol) was dissolved in dry DMF (25 mL) and treated with NaH (156 mg, 6.50 mmol). After the evolution of gas ceased (~30 min), propargyl bromide (1.8 mL of 80% wt solution in PhMe, 16.0 mmol) was added via a syringe. The mixture was stirred at 23 °C for 3 d. MeOH (2.0 mL) was added and the solvents were removed in vacuo. The crude brown oil was filtered through a plug of silica, eluting with Me_2CO, to provide pure **9c** (1.39 g, 95%) as a brown oil. **9c**: MS (FAB+): *m/z* (rel intensity) = 588 (M^+, 100%), 391 (33). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, ^3J (H,H) = 8.5 Hz, 2H), 7.33 (t, ^3J (H,H) = 8.4 Hz, 2H), 6.83 (d, ^3J (H,H) = 8.4 Hz, 2H), 4.29–4.27 (m, 4H), 4.17 (d, ^4J (H,H) = 2.4 Hz, 4H), 4.00–3.95 (m, 4H), 3.80–3.78 (m, 4H), 3.70–3.67 (m, 4H), 3.67–3.63 (m, 16H), 2.41 (t, ^4J (H,H) = 2.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.22, 126.65, 124.98, 114.51, 105.55, 79.56, 74.44, 70.89, 70.60, 70.53, 70.51, 70.29, 69.72, 69.00, 67.81, 58.29. HRMS Calcd for $C_{32}H_{44}O_{10}$: 588.2934. Found: 588.2942.

Scheme S8. Attempted Synthesis of Catenane **1a** · $4PF_6$.



The DNP derivative **8a** (9.2 mg, 0.024 mmol), **CBPQT** · $4PF_6$ (22.0 mg, 0.02 mmol), and CuI (2.0 mg, 0.01 mmol) were dissolved in CD_3CN (0.6 mL) and transferred into an NMR tube. The purple solution was left at 23 °C for 2 d. After this time, ^{1}H NMR spectroscopy and FAB MS showed no sign of formation of **1a** · $4PF_6$. Performing the reaction with a $CuSO_4 \cdot 5H_2O$ / ascorbic acid catalyst mixture gave identical results.

Scheme S9. Synthesis of Catenane **1c** · $4PF_6$.

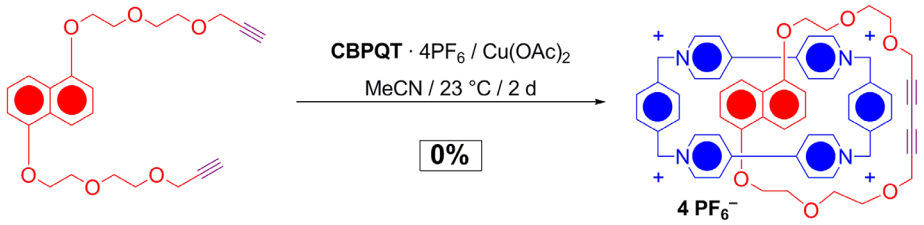


8c **1c** · $4PF_6$

The DNP derivative **8c** (34.5 mg, 0.06 mmol), **CBPQT** · $4PF_6$ (44.0 mg, 0.04 mmol), and CuI (11.5 mg, 0.06 mmol) were suspended in CD_3CN (0.6 mL) and transferred into an NMR tube. The purple solution was allowed to stand at 23 °C for 3 d. After this time, the ^{1}H NMR spectroscopy showed peaks consistent with the presence of **1c** · $4PF_6$. The reaction mixture was filtered through a plug of silica (gradient elution: Me_2CO → 2% solution of NH_4PF_6 in Me_2CO). Purple fractions were collected, concentrated to a minimum volume and the crude catenane **1c** · $4PF_6$ was precipitated by the addition of H_2O. After filtration and drying, this crude material was analyzed and showed to contain **CBPQT** · $4PF_6$ and the desired [2]catenane **1c** · $4PF_6$. The crude mixture was dissolved in minimum amount of Me_2CO and hexane was added dropwise until precipitation of **CBPQT** · $4PF_6$ occurred. Removal of the solvent from the supernatant provided pure **1c** · $4PF_6$ (15 mg, 23%) as a purple solid, mp 199–201 °C with decomp. **1c** · $4PF_6$: MS (ESI): *m/z* (rel intensity) = 1530 ([**1c** · $3PF_6$]$^+$, 8%), 692 ([**1c** · $2PF_6$]$^{2+}$, 100), 413 ([**1c** · PF_6]$^{3+}$, 45). ^{1}H NMR (500 MHz, DMF-d_7, 270 K): δ 9.73 (br d, 1H, α-CBPQT^{4+}-H), 9.48 (d, ^3J (H,H) = 6.5 Hz, 1H, α-CBPQT^{4+}-H), 9.46 (d, ^3J (H,H) = 6.6 Hz, 1H, α-CBPQT^{4+}-H), 9.44-9.34 (br m, 2H, α-CBPQT^{4+}-H), 9.32 (d, ^3J (H,H) = 6.8 Hz, 1H, α-CBPQT^{4+}-H), 9.28 (d, ^3J (H,H) = 6.7 Hz, 1H, α-CBPQT^{4+}-H), 8.81 (br s, 1H, α-CBPQT^{4+}-H), 8.31–8.09 (m, 8H, β-CBPQT^{4+}-H), 7.85 (br m, 2H, aryl-CBPQT^{4+}-H), 7.82 (br s, 2H, aryl-CBPQT^{4+}-H), 7.72 (br s, 2H, aryl-CBPQT^{4+}-H), 7.62 (br s, 2H, aryl-CBPQT^{4+}-H), 7.46 (s, 1H, triazole-H), 6.29 (d, ^3J (H,H) = 7.9 Hz, 1H, DNP aryl-H *o*-O), 6.10–5.91 (m, 11H, DNP aryl-H *o*-O, DNP aryl-H *m*-O, and CBPQT^{4+} benzyl-H), 4.18–2.69 (m, 32H), 3.03 (s, 2H, propargyl-H), 2.54 (d, ^3J (H,H) = 7.7 Hz, 1H, DNP aryl-H *p*-O), 2.53 (d, ^3J (H,H) = 8.0 Hz, 1H, DNP

aryl-H *p*-O). HRMS Calcd for $C_{65}H_{73}N_7O_9P_2F_{12}$ ([**1c** · $2PF_6$]$^{2+}$): 692.7389. Found: 692.7350.

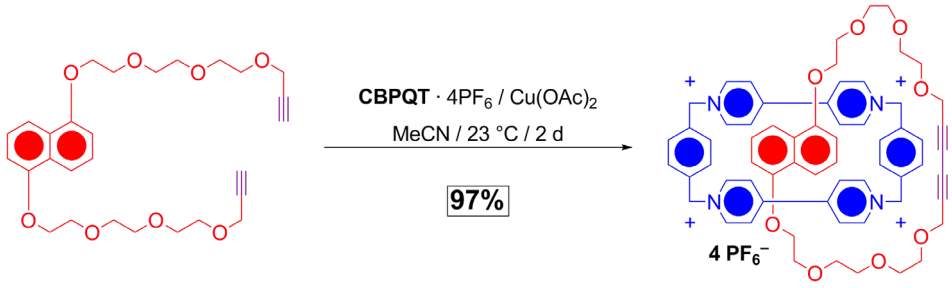
Scheme S10. Attempted Synthesis of Catenane **2a** · $4PF_6$.



9a **2a** · $4PF_6$

The DNP derivative **9a** (50.0 mg, 0.12 mmol), **CBPQT** · $4PF_6$ (44.0 mg, 0.04 mmol), and $Cu(OAc)_2$ · H_2O (40.0 mg, 0.20 mmol) were dissolved in MeCN (30 mL). The deeply bluish-purple solution was stirred at 23 °C for 2 d. The solvent was removed in vacuo, and the crude purple solid was subjected to column chromatography on silica (Me_2CO → 2% solution of NH_4PF_6 in Me_2CO). Several fractions were collected, concentrated to a small volume, and precipitated by addition of cold H_2O. None of the materials isolated by filtration contained any evidence for the presence of **2a** · $4PF_6$ (by ^{1}H NMR spectroscopy and FAB MS). Additionally, although **2a** · $4PF_6$ was expected to be purple, all of the collected fractions were either colorless or pale yellow.

Scheme S11. Improved Synthesis of Catenane **2b** · $4PF_6$.

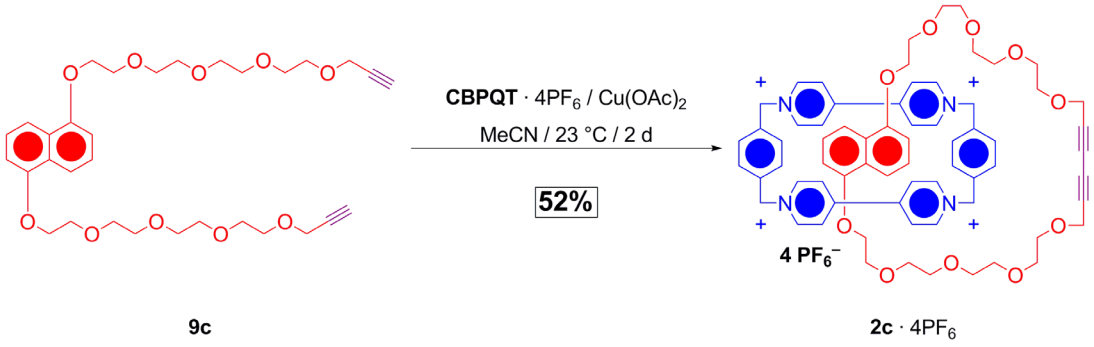


9b **2b** · $4PF_6$

The DNP derivative **9b** (60.0 mg, 0.12 mmol), **CBPQT** · $4PF_6$ (44.0 mg, 0.04 mmol), and $Cu(OAc)_2$ · H_2O (40.0 mg, 0.20 mmol) were dissolved in MeCN (30 mL). The deeply bluish-purple solution was stirred at 23 °C for 2 d. The solvent was removed in vacuo, and

the crude purple solid was subjected to column chromatography on silica (Me_2CO → 2% solution of NH_4PF_6 in Me_2CO). Purple fractions were collected and reduced to minimal volume. Cold H_2O was added to precipitate the purple solid. After filtration and drying, 58 mg (97%) of **2b** · $4PF_6$ was obtained. The spectroscopic data for this sample were identical to one previously reported.[S6] The amount of **2b** · $4PF_6$ prepared allowed the collection of ^{13}C NMR spectrum. **2b** · $4PF_6$: ^{13}C NMR (125 MHz, CD_3CN): δ 151.00, 145.12, 144.37, 136.48, 131.29, 131.07, 128.02, 125.92, 124.45, 124.35, 108.27, 104.12, 70.75, 70.54, 70.12, 69.70, 69.48, 68.25, 67.84, 57.89.

Scheme S12. Synthesis of Catenane **2c** · $4PF_6$.



The DNP derivative **9c** (72.0 mg, 0.12 mmol), **CBPQT** · $4PF_6$ (44.0 mg, 0.04 mmol), and $Cu(OAc)_2$ · H_2O (40.0 mg, 0.20 mmol) were dissolved in MeCN (30 mL). The deeply bluish-purple solution was stirred at 23 °C for 2 d. The solvent was removed in vacuo, and the crude purple solid was subjected to column chromatography on silica (Me_2CO → 1% solution of NH_4PF_6 in Me_2CO). Purple fractions were collected and concentrated to dryness. Cold H_2O was added to precipitate the purple solid. After filtration and drying, this crude material was analyzed and showed to contain **CBPQT** · $4PF_6$ and the desired **2c** · $4PF_6$. The crude mixture was dissolved in minimal amount of acetone and hexane was added dropwise until precipitation of **CBPQT** · $4PF_6$ occurred. Removal of the solvent from the supernatant provided pure **2c** · $4PF_6$ (35 mg, 52%) as a purple solid, mp >230 °C without decomp. **2c** · $4PF_6$: MS (ESI): *m/z* (rel intensity) = 1541 ([**2c** · $3PF_6$]$^+$, 1%), 698 ([**2c** · $2PF_6$]$^{2+}$, 62), 563 (100), 417 ([**2c** · PF_6]$^{3+}$, 31). ^1H NMR (500 MHz, CD_3CN): δ 9.01 (br s, 2H, α-CBPQT^{4+}-H), 8.86 (br s, 4H, α-CBPQT^{4+}-H), 8.65 (br s, 2H, α-CBPQT^{4+}-H), 8.02 (br s, 8H, β-CBPQT^{4+}-H), 7.34 (br s, 8H, aryl-CBPQT^{4+}-H), 6.27 (d, ^3J (H,H) = 7.8

Hz, 2H, DNP aryl-H *o*-O), 6.02 (t, ^{3}J (H,H) = 8.0 Hz, 2H, DNP aryl-H *m*-O), 5.74 (br s, 8H, $CBPQT^{4+}$ benzyl H), 4.31 (m, 4H), 4.17 (m, 4H), 4.02 (m, 4H), 3.89 (m, 4H), 3.85 (s, 4H, propargyl-H), 3.73 (m, 2H), 3.56 (m, 2H), 3.40 (m, 2H), 3.19 (m, 2H), 2.50 (br s, 2H, DNP aryl-H *p*-O). HRMS Calcd for $C_{68}H_{74}N_4O_{10}P_2F_{12}$ ($[\mathbf{6} \cdot 2PF_6]^{2+}$): 698.2350. Found: 698.2326.

X-Ray Diffraction: Data Collection and Refinement Parameters

[**9a** ⊂ **CBPQT**] · $4PF_6$: $C_{60}H_{60}F_{24}N_4O_6P_4$, crystal size 0.20 × 0.20 × 0.15 mm^3, space group $P\bar{1}$, scan range 8.0 < 2θ < 56.6°, T = 100(2) K, a = 10.163(3), b = 12.669(4), c = 14.245(5) Å, α = 99.963(4), β = 107.120(3), γ = 112.522(3), V = 1531.9(9) $Å^3$, Z = 1, ρ_{calcd} = 1.640 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.253 mm^{-1}, 7331 unique reflections, of which 5083 were taken as observed [I>2σ(I)], R(F) = 0.059, $wR(F^2)$ = 0.155 (all data).

1b · $4PF_6$: $C_{73}H_{83}F_{24}N_{13}O_7P_4$, crystal size 0.60 × 0.40 × 0.05 mm^3, space group $P\bar{1}$, scan range 7.8 < 2θ < 53.1°, T = 100(2) K, a = 15.304(7), b = 15.316(7), c = 21.776(14) Å, α = 95.059(7), β = 106.489(7), γ = 116.953(5), V = 4220(4) $Å^3$, Z = 2, ρ_{calcd} = 1.444 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.201 mm^{-1}, 17307 unique reflections, of which 7251 were taken as observed [I>2σ(I)], R(F) = 0.076, $wR(F^2)$ = 0.239 (all data).

2b · $4PF_6$: $C_{76}H_{84}F_{24}N_{10}O_8P_4$, crystal size 0.50 × 0.40 × 0.20 mm^3, space group $P\bar{1}$, scan range 8.4 < 2θ < 59.7°, T = 100(2) K, a = 13.690(2), b = 13.848(2), c = 24.046(4) Å, α = 84.815(2), β = 85.732(2), γ = 67.626(2), V = 4194.3(11) $Å^3$, Z = 1, ρ_{calcd} = 1.461 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.203 mm^{-1}, 23132 unique reflections, of which 17155 were taken as observed [I>2σ(I)], R(F) = 0.076, $wR(F^2)$ = 0.222 (all data).

2c · $4PF_6$: $C_{80}H_{92}F_{24}N_{13}O_{10}P_4$, crystal size 0.60 × 0.30 × 0.10 mm^3, space group $P\bar{1}$, scan range 7.8 < 2θ < 56.5°, T = 100(2) K, a = 14.021(3), b = 14.121(3), c = 22.210(5) Å, α = 94.628(2), β = 93.400(2), γ = 93.554(3), V = 4365.5(17) $Å^3$, Z = 2, ρ_{calcd} = 1.470 gcm^{-3}, $\mu(MoK_\alpha)$ = 0.200 mm^{-1}, 20861 unique reflections, of which 13530 were taken as observed [I>2σ(I)], R(F) = 0.085, $wR(F^2)$ = 0.275 (all data).

Supramolecular Organization of Crystallographically Characterized Materials

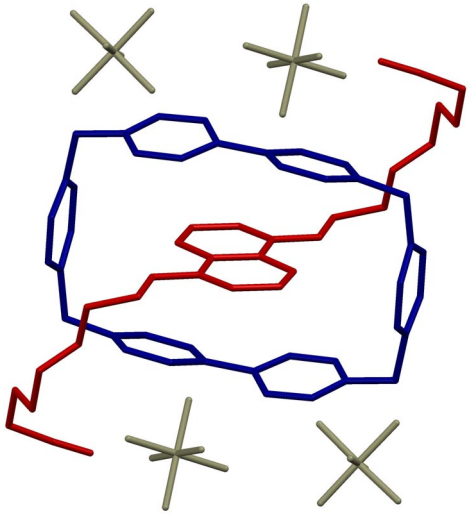


Figure S1. Unit cell contents of [2]pseudorotaxane **[**9a ⊂ CBPQT**]**$^{4+}$. Donor rings shown in red, acceptor rings in blue, PF_6^- counterions in gray. Aside from the remaining PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

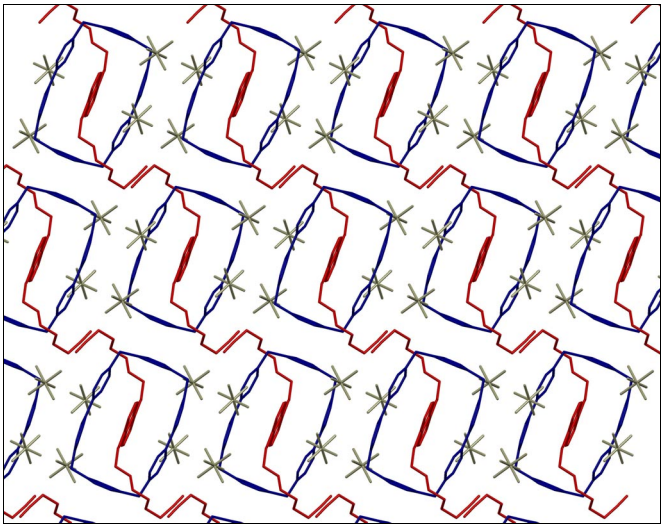


Figure S2. Section of the packing diagram of [2]pseudorotaxane [**9a** ⊂ **CBPQT**]$^{4+}$, viewed down the crystallographic *a* axis. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

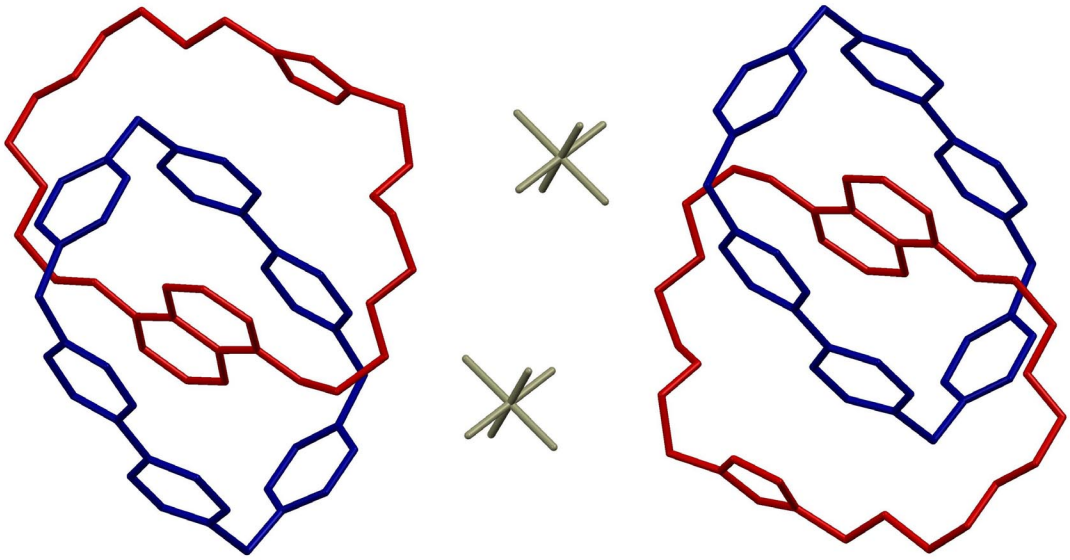


Figure S3. Unit cell contents of [2]catenane **1b**$^{4+}$. Donor rings shown in red, acceptor rings in blue, bridging PF_6^- counterions in gray. Aside from the remaining PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

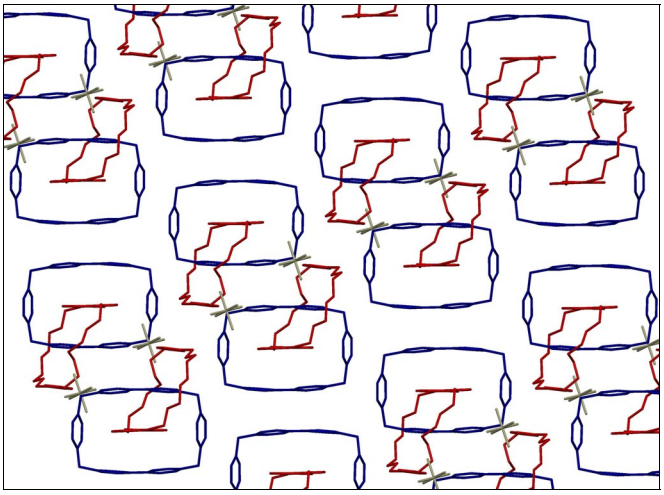


Figure S4. Section of the packing diagram of [2]catenane **1b**$^{4+}$. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

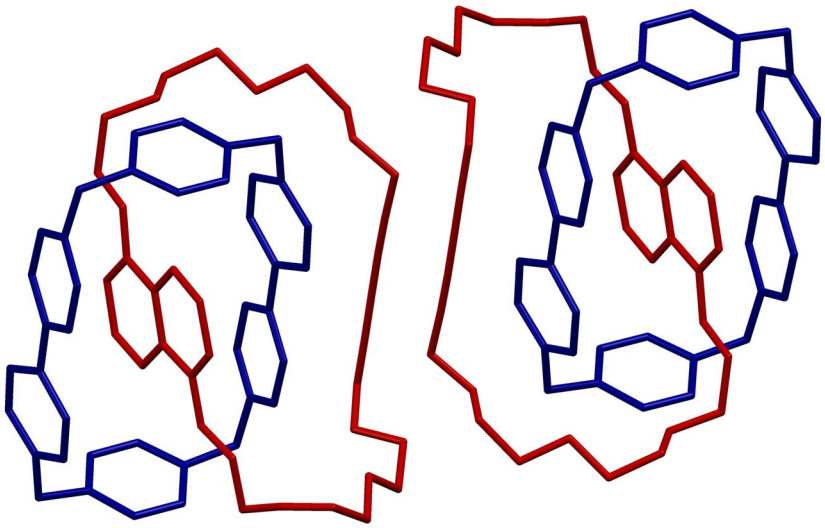


Figure S5. Unit cell contents of [2]catenane **2b**$^{4+}$. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

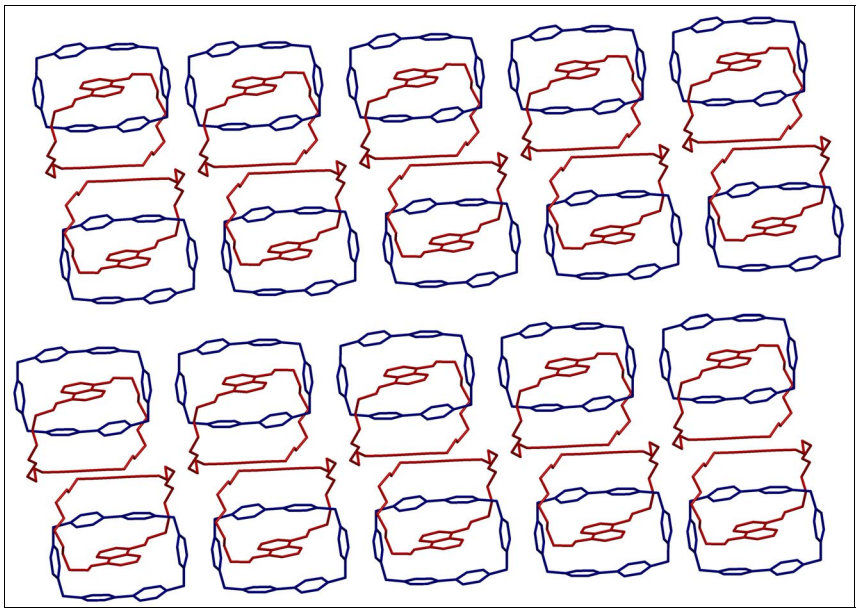


Figure S6. Section of the packing diagram of [2]catenane **2b**$^{4+}$. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

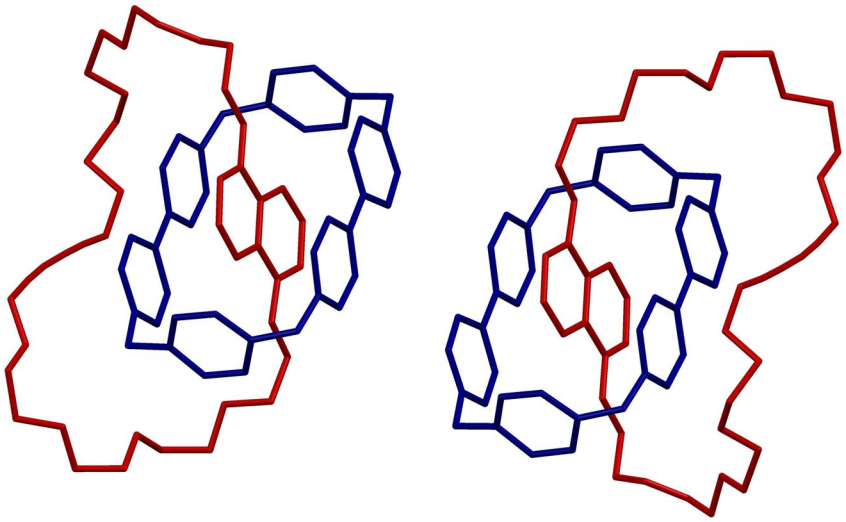


Figure S7. Unit cell contents of [2]catenane **2c**$^{4+}$. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

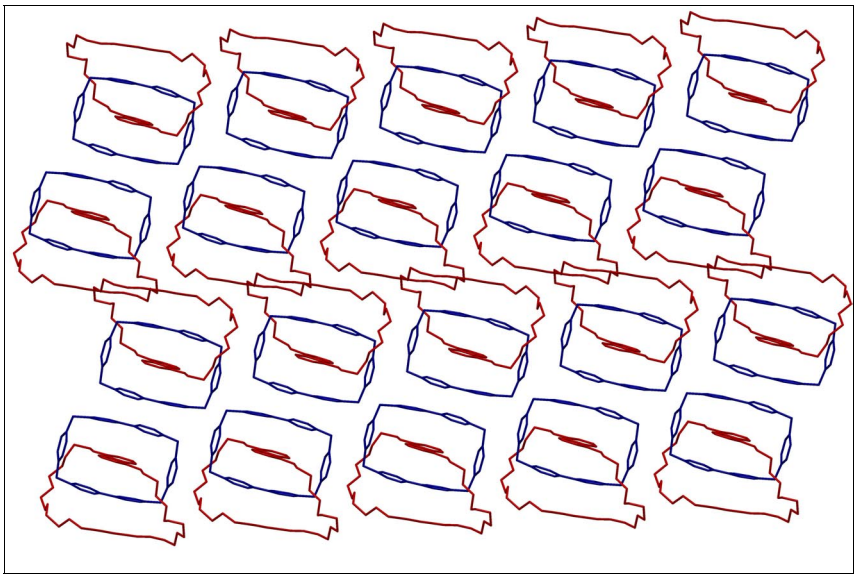


Figure S8. Section of the packing diagram of [2]catenane **2c**$^{4+}$. Donor rings shown in red, acceptor rings in blue. Aside from PF_6^- counterions, hydrogen atoms and solvent molecules were omitted for clarity.

Partial VT-NMR spectra of [2]catenanes 1b,c · $4PF_6$ and 2b,c · $4PF_6$

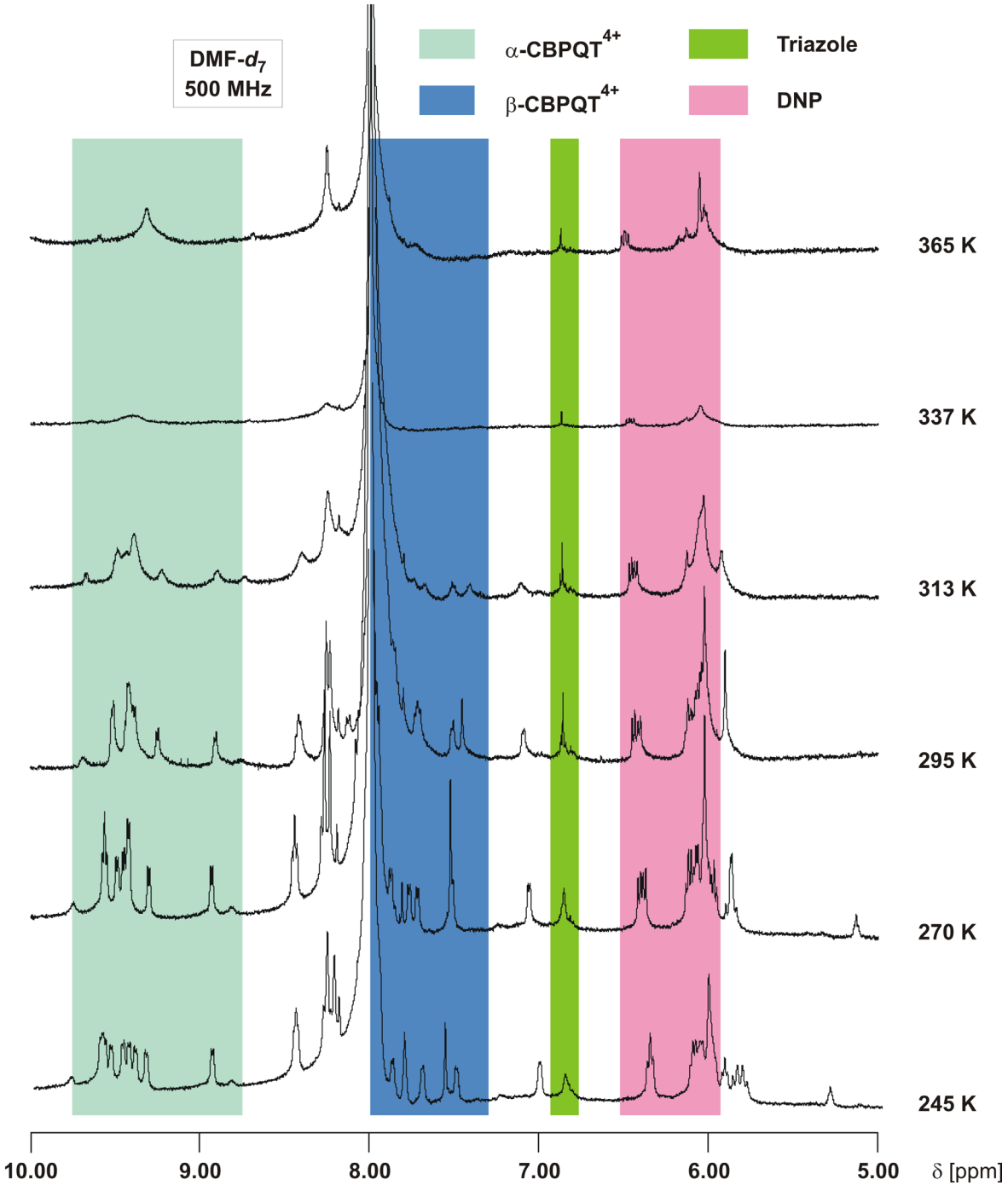


Figure S9. VT-NMR spectra of **1b** · $4PF_6$ (DMF-d_7).

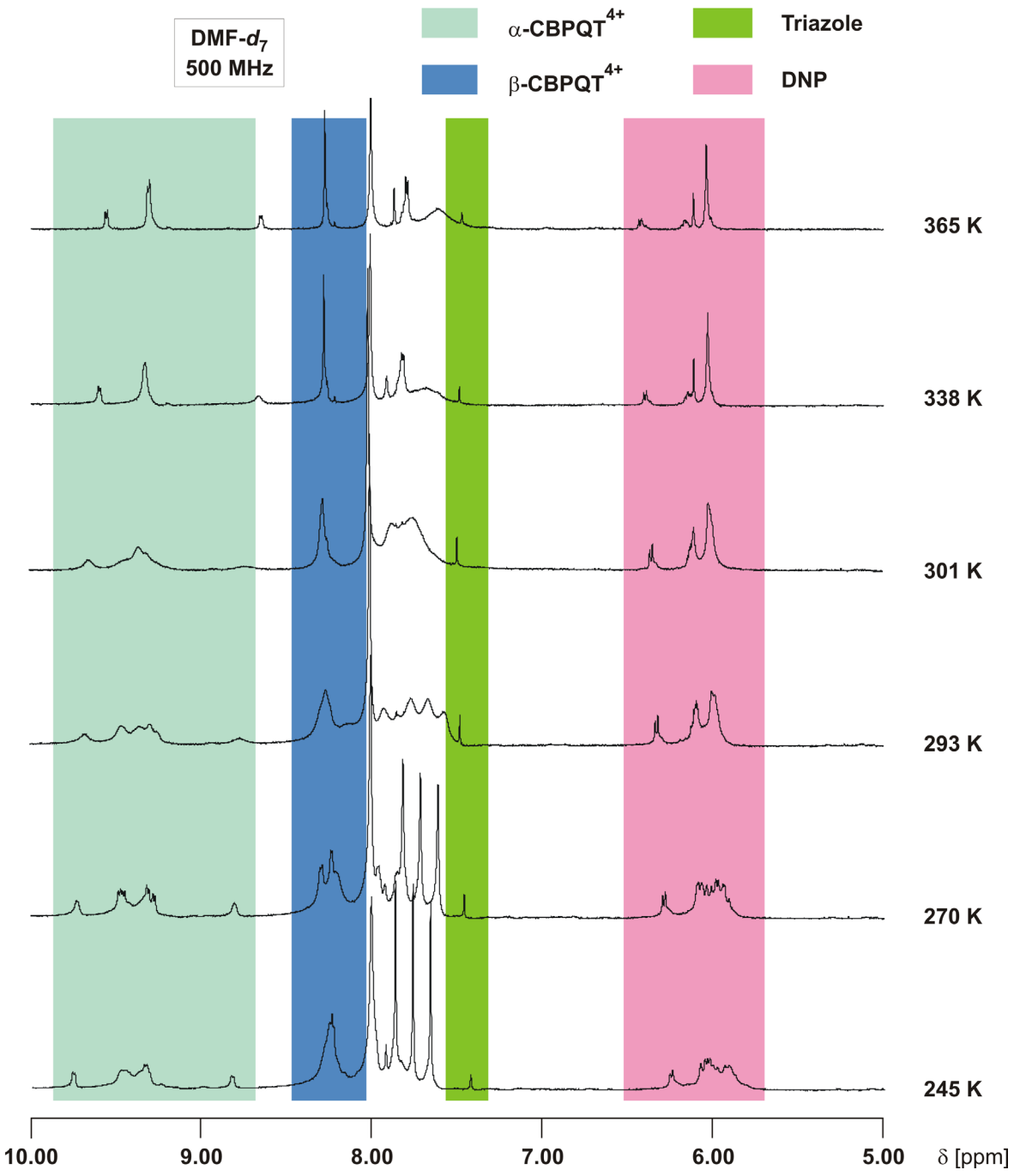


Figure S10. VT-NMR spectra of **1c** · $4PF_6$ (DMF-d_7).

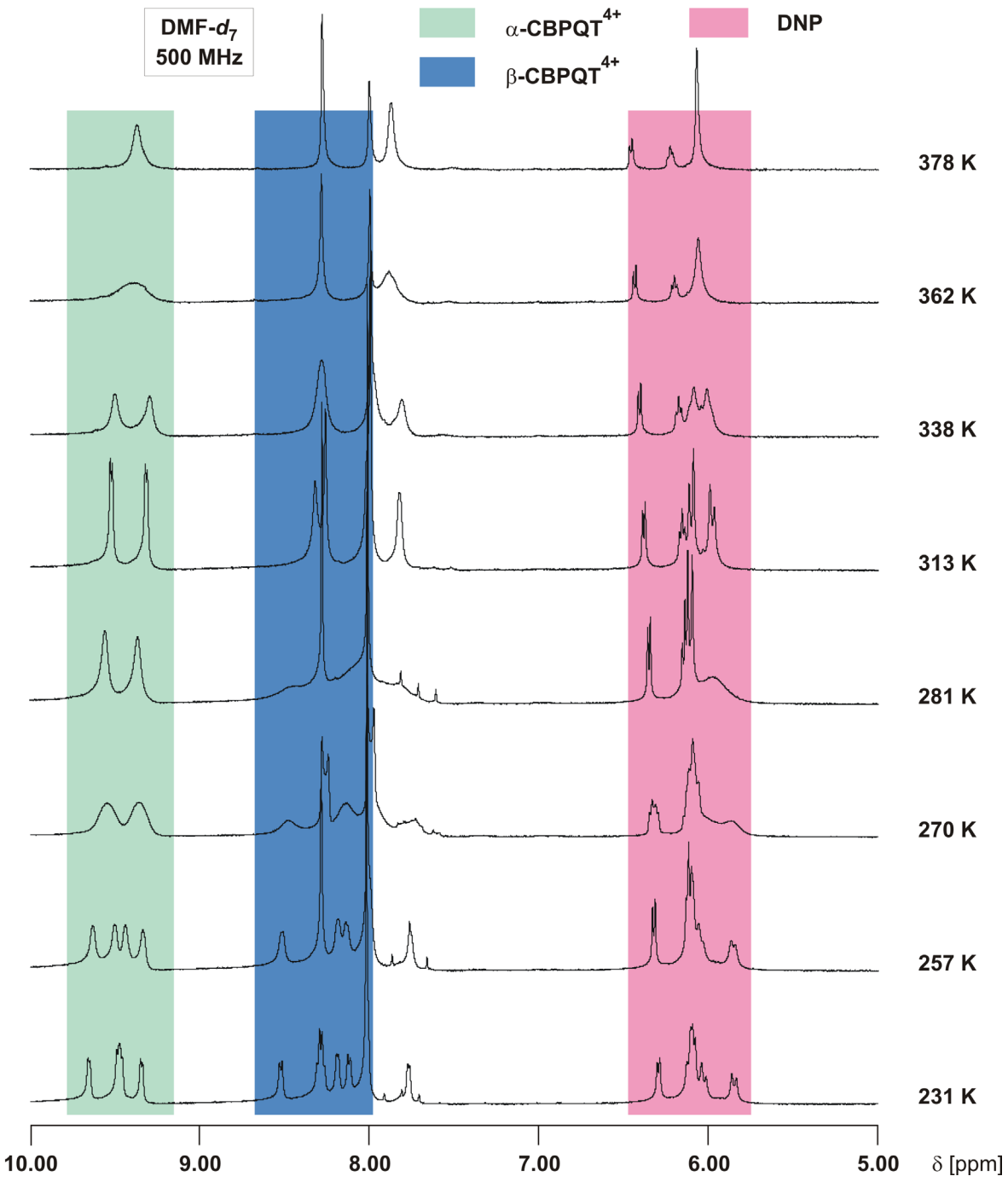


Figure S11. VT-NMR spectra of **2b** · $4PF_6$ (DMF-d_7).

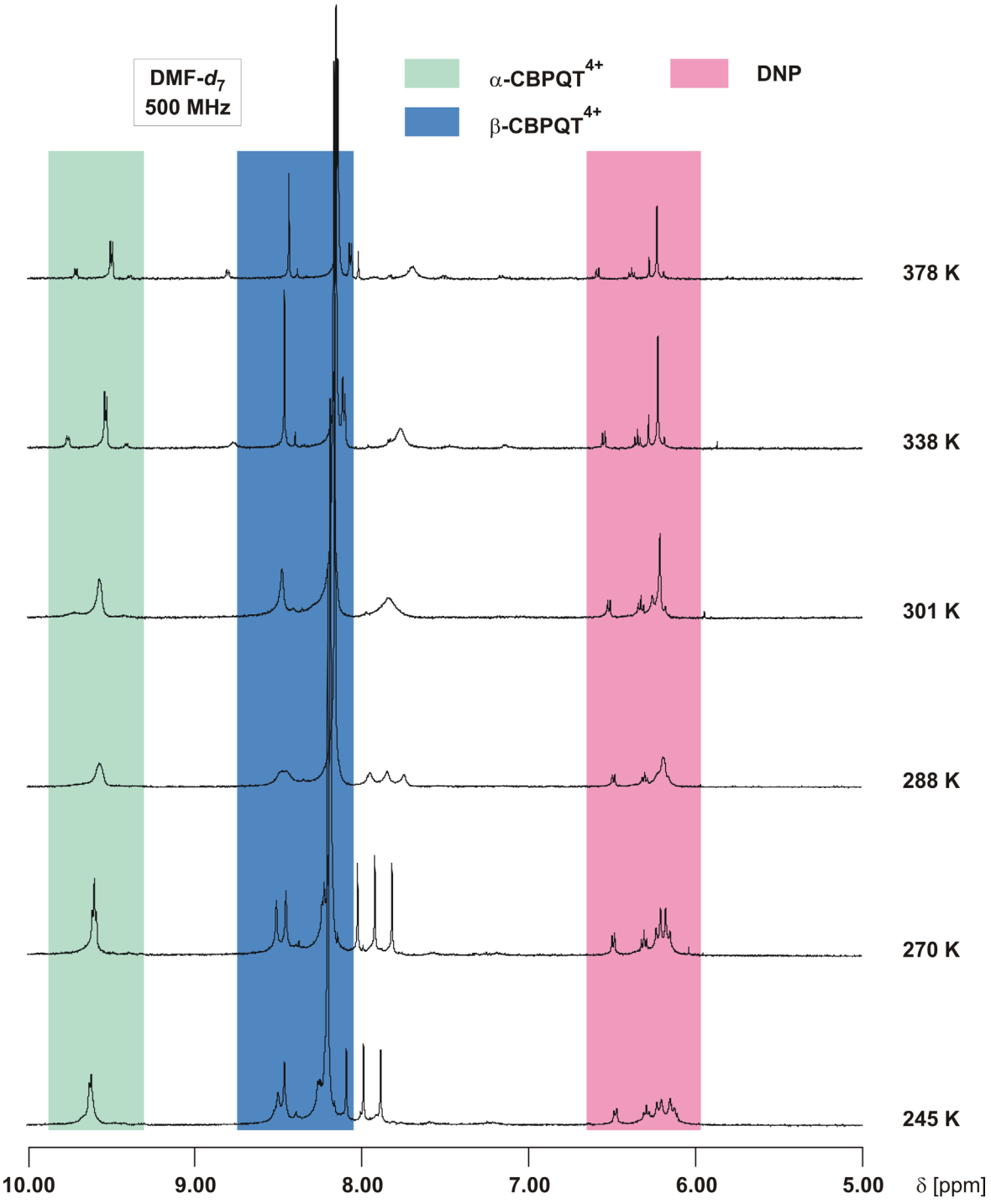


Figure S12. VT-NMR spectra of **2c** · $4PF_6$ (DMF-d_7).

References

(S1) Asakawa, M.; Dehaen, W.; L'abbé, G.; Menzer, S.; Nouwen, J.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Org. Chem.* **1996**, *61*, 9591–9595.

(S2) Amabilino, D. B.; Anelli, P.-L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142–11170.

(S3) Ashton, P. R.; Huff, J.; Menzer, S.; Parsons, I. W.; Preece, J. A.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1996**, *2*, 31–44.

(S4) Collier, C. P.; Jeppesen, J. O.; Liu, Y.; Perkins, J.; Wong, E. W.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 12632–12641.

(S5) Liu, Y.; Saha, S.; Vignon, S. A.; Flood, A. H.; Stoddart, J. F. *Synthesis* **2005**, 3437–3455.

(S6) Miljanić, O. Š.; Dichtel, W. R.; Mortezaei, S.; Stoddart, J. F. *Org. Lett*. **2006**, *8*, 4835–4838.

Full References from the Manuscript

(6j) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halprin, E.; DeIonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, *445*, 414–417.

(11c) Anelli, P.-L. Masumi Asakawa, M.; Ashton, P. R.; Bissell, R. A.; Clavier, G.; Górski, R.; Kaifer, A. E.; Langford, S. J.; Mattersteig, G.; Menzer, S.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *Chem.–Eur. J.* **1997**, *3*, 1113–1135.

(12c) Anelli, P.-L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, *M. T.;* Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193–218.

(14) Ashton, P. R.; Brown, C. L.; Chrystal, E. J. T.; Goodnow, T. T.; Kaifer, A. E.; Parry, K. P.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 634–639.

(15c) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams D. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 333–337.

(30a) Amabilino, D. B.; Anelli, P.-L.; Ashton, P. R.; Brown, G. R.; Córdova, E.; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142–11170.

(33) Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Gillard, R. E.; Kocian, O.; Raymo, F. M.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1997**, *62*, 26–37.

(48b) Ashton, P. R.; Balzani, V.; Credi, A.; Kocian, O.; Pasini, D.; Prodi, L.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem.–Eur. J.* **1998**, *4*, 590–607.

(49a) Liu, Y.; Flood, A. H.; Bonvallett, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H. R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C. M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745–9759.

(49b) Huang, T. J.; Brough, B.; Ho, C.-M.; Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Tseng, H.-R.; Stoddart, J. F.; Baller, M.; Magonov, S. *Appl. Phys. Lett.* **2004**, *85*, 5391–5393.